



Challenge

Reliable and easy to use fast multi-element analysis of major and minor elements in digests of lithium ore samples

Solution

Fast-sequential High-Resolution Continuum-Source (HR-CS) Flame-AAS contrAA 800 F/D, equipped with the autosampler AS-FD with automatic dilution function

Intended audience

Raw material exploration sector with focus on lithium

Fast Analysis of Lithium Ore Using Flame-AAS contrAA 800 F/D

Introduction

Environmentally friendly energy storage devices like lithium-ion batteries play a crucial role and subsequently, the economic importance of lithium is increasing. The primary sources of lithium are brine deposits from salars or geothermal fields, as well as clays, granites, and granite-related pegmatites. While salar deposits hold the largest reserves of lithium, lithium-rich mineral concentrates from pegmatites are currently the main source of production due to their higher quality and lower costs. ^[1]

To extract lithium and convert it into industrial compounds, the main and minor components of geological, lithium-containing materials need to be determined. While the lithium content is the most important factor, the presence and concentration of other elements are also relevant and require further processing methods. Traditional exploration methods can be costly and time-consuming, requiring extensive drilling and analysis. In contrast, the pathfinder element approach allows for quicker and more affordable exploration by analyzing soil and rock samples.

Several methods for analyzing lithium ore include different sample preparation procedures (fusion, multi-acid digestion on hot plate) for each targeted element (e.g., Ca, Fe, Li, Mn) and recommend three different techniques for sample analysis: flame atomic absorption spectrometry (AAS), inductively coupled optical emission spectrometry (ICP-OES) as well as photometry, and complexation with ethylenediaminetetraacetic acid (EDTA).

The objective of this research is to simplify and expedite the overall analytical procedure for analyzing major and minor elements in lithium ore samples by exploring alternative sample preparation methods. The contrAA 800 F/D, a high-resolution continuum source flame atomic absorption spectrometer combines the advantages of flame AAS technique and ICP-OES and, therewith, it is utilized for the analysis, taking advantage of its multi-element capability and reducing the complexity of the measurement process. Additionally, the speedwave XPERT microwave digestion system is employed to decrease the overall time and acid volumes required for sample preparation.

Materials and Methods

Samples and reagents

Certified reference materials

- Pegmatite Li Ore – CRM Oreas 750
- Pegmatite Li Ore – CRM Oreas 753
- Li Concentrate (Spodumene) – CRM Oreas 999

Reagents

- HNO₃ (65%, p.a., Carl Roth)
- HCl (32%, p.a., VWR)
- H₂SO₄ (95%, p.a., VWR)
- HF (38-40%, extra pure, Merck)
- CsCl (≥99.999%, p.a., Carl Roth) for preparation of a 10% (m/v) solution in deionized water
- Single element standards for AAS (1 g/L Al, Ca, Fe, K, Li, Mg, Mn and Na, Merck)

Sample preparation

For the development of a suitable microwave assisted digestion procedure two acid mixture variations have been used and compared for digestion effectivity for the observed elements:

Method A: 4 mL H₂SO₄, 2 mL HF, 1 mL HCl, 2 mL HNO₃

Method B: 2 mL H₂SO₄, 1 mL HF, 1 mL HCl, 6 mL HNO₃

The digestion was performed by using a Speedwave XPERT microwave system and DAK100 vessels. Up to 0.15 g of each sample was accurately weighed into the digestion vessel and the acids (mixtures as described before) were added.

The mixture was swirled carefully and left standing for at least 10 minutes before the vessel was closed. Subsequent heating was performed stepwise (210 °C for 10 min, 230 °C

for 10 min, 240 °C for 30 min). Afterwards the vessels were allowed to cool to room temperature and each solution was transferred into a graduated PP-vial and filled to 50 mL with deionized water.

Since Al and Ca form insoluble fluorine compounds, leading to inferior recoveries, a subsequent complexation with H₃BO₃ (1 g per 1 mL HF, 15 min at 190 °C) was performed.

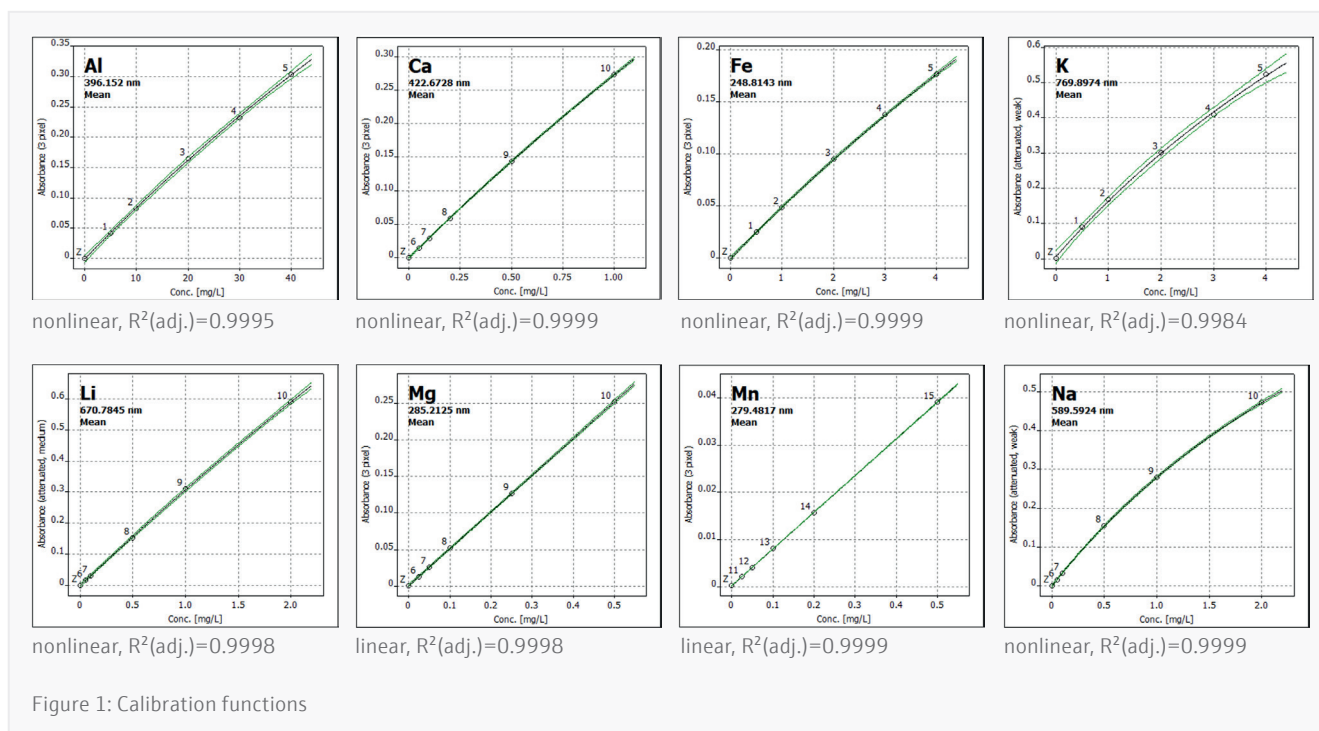
The applied procedures led to a clear solution with a white precipitation. Therefore, the solutions were centrifuged (3500 rpm, 5 min) and the supernatant was used to prepare the test sample solutions. For measurement each sample solution was pre-diluted manually by a factor of 20 with 2% (v/v) HNO₃ and 0.2% (m/v) CsCl to match the calibration range and overcome possible matrix related non-spectral interferences on the signal intensity of the observed elements. In the event the calibration range was exceeded, the intelligent overrange dilution function of the autosampler AS-FD was applied.

Calibration

All quantitative measurements were carried out against external calibration curves. Calibration levels for each element were chosen based on expected concentration range. The calibration standards were prepared automatically by the flame autosampler AS-FD by dilution of manually prepared stock solutions using 2% (v/v) HNO₃ and 0.2% (m/v) CsCl as a diluent. The element concentrations of the stock solution and the prepared working standards are given in Table 1. The resulting calibration functions used for quantification are shown in Figure 1.

Table 1: Concentrations of the calibration standards

Standard	Concentration [mg/L]							
	Al	Ca	Fe	K	Li	Na	Mg	Mn
Stock	100	5	25	25	5	5	2.5	2.5
Cal. 0	0	0	0	0	0	0	0	0
Cal. Std. 1	5	0.05	0.25	0.5	0.05	0.05	0.025	0.025
Cal. Std. 2	10	0.1	0.5	1.0	0.1	0.1	0.05	0.05
Cal. Std. 3	20	0.2	1.0	2.0	0.5	0.5	0.10	0.10
Cal. Std. 4	30	0.5	2.5	3.0	1.0	1.0	0.25	0.20
Cal. Std. 5	40	1.0	5.0	4.0	2.0	2.0	0.50	0.50



Instrumentation and method parameters

The analysis was performed on the High-Resolution Continuum-Source (HR-CS) Flame AAS contrAA 800 F/D, equipped with an autosampler with automatic dilution function. Individual settings and components are summarized in Table 2. Detailed information about the method parameters and settings are listed in Table 3.

Table 2: Common instrument configuration and settings

Parameter	Specification
Instrument	contrAA 800 F/D
Burner head	50 mm
Burner angle	0°
Autosampler	AS-FD
Additional accessories	SFS 6, Scraper (for N ₂ O flame)

Table 3: Method parameters

Element	Wavelength [nm]	Meas. Time [s]	Burner height [mm]	Flame type	Fuel gas [L/h]	Aux. Oxidant [L/h]	Eval. pixels	Correction
Al	396.1520	3	6	C ₂ H ₂ /N ₂ O	240	0	3	IBC
Ca	422.6728	3	8	C ₂ H ₂ /N ₂ O	230	0	3	IBC
Fe	248.3270	3	8	C ₂ H ₂ /air	85	150	3	IBC
K	769.8974	3	6	C ₂ H ₂ /air	60	75	att. (weak)	IBC
Li	670.7845	3	6	C ₂ H ₂ /air	65	75	att. (medium)	IBC
Mg	285.2125	3	4	C ₂ H ₂ /N ₂ O	180	0	3	IBC, perm. str.
Mn	279.4817	3	4	C ₂ H ₂ /N ₂ O	180	0	3	IBC, perm. str.
Na	589.5924	3	5	C ₂ H ₂ /air	55	75	att. (weak)	IBC

IBC: Iterative Baseline Correction

perm. str.: Automatic correction of permanent absorption structures (e.g., by the diluent or flame gases)

att.: Signal attenuation by side pixel evaluation

Results and Discussion

The analysis of three CRMs was used to perform method development and validation. Most of the determined elements in the observed CRMs were found in a recovery range between 90 - 110% for both digestion attempts (see Figure 2). Both digestion procedures led to comparable results and concurring results of the digestion replicates demonstrate the reproducibility of the sample preparation procedure. Rather, the recovery rates of the samples, shown in Figure 2, indicate which one of the two digestion procedures is most appropriate for which element. In existing standards, the acidic digestion is performed on hot plate using HF and H₂SO₄. This approach was adapted, scaled down to the microwave system and extended to include additional acids in order to stabilize all analytes appropriately in solution. Since lithium ores contain oxides of silica, aluminum and many of their variations or mixtures, digestion with varying mixtures of sulfuric, hydrofluoric, nitric and hydrochloric acid were tested for their efficiency. Since hydrofluoric acid can lead to a significant analyte loss by precipitation of insoluble fluorides (e.g., Al, Ca), a subsequent complexation step with boric acid was found to be mandatory for a reliable recovery of the observed elements. For each CRM sample the digestion was carried out in duplicates (Replicate #1 and #2) for observation of the reproducibility of the methods. The measurement results for the two applied digestion mixtures (Method A and B) are listed in Tables 4 and 5.

Table 4: Measuring results - Method A

Sample (CRM)	Element	DF	Certified value [wt%]	Replicate #1		Replicate #2	
				Measured value [wt%]	RSD _(n=3) [%]	Measured value [wt%]	RSD _(n=3) [%]
Oreas 750	Al	20	5.42	5.22	0.5	5.23	0.3
	Ca	20	0.83	0.812	0.5	0.806	0.4
	Fe	20	1.67	1.59	0.6	1.66	0.2
	K	20	1.69	1.57	0.5	1.64	0.2
	Li	20	0.23	0.225	1.1	0.217	0.7
	Mg	20	0.32	0.322	0.4	0.321	1.8
	Mn	20	0.04	0.040	1.2	0.037	1.8
	Na	20*	1.53	1.47	0.9	1.51	1.2
Oreas 753	Al	20	8.22	7.99	0.6	7.94	0.5
	Ca	20	0.11	0.104	0.3	0.106	0.7
	Fe	20	0.84	0.797	0.7	0.777	1.3
	K	20	1.93	1.80	0.6	1.78	1.7
	Li	20	0.99	0.968	0.9	0.942	1.8
	Mg	20	0.011	0.012	2.4	0.013	0.9
	Mn	20	0.07	0.077	0.3	0.074	1.7
	Na	20*	2.16	2.24	0.8	2.10	0.9
Oreas 999	Al	20	10.77	11.19	0.6	11.3	0.5
	Ca	20	0.45	0.432	0.5	0.44	0.4
	Fe	20	1.62	1.64	1.4	1.64	2.0
	K	20	0.50	0.465	2.0	0.48	2.5
	Li	20*	2.65	2.61	1.2	2.55	1.4

Sample (CRM)	Element	DF	Certified value [wt%]	Replicate #1		Replicate #2	
				Measured value [wt%]	RSD _(n=3) [%]	Measured value [wt%]	RSD _(n=3) [%]
Oreas 999	Mg	20*	0.410	0.443	0.9	0.457	1.2
	Mn	20	0.143	0.141	1.6	0.148	0.7
	Na	20	0.693	0.639	1.9	0.681	1.8

RSD: Relative standard deviation (3 measurement replicates)

DF: Manual pre-dilution factor

*additional autosampler dilution due to exceeding the calibration range

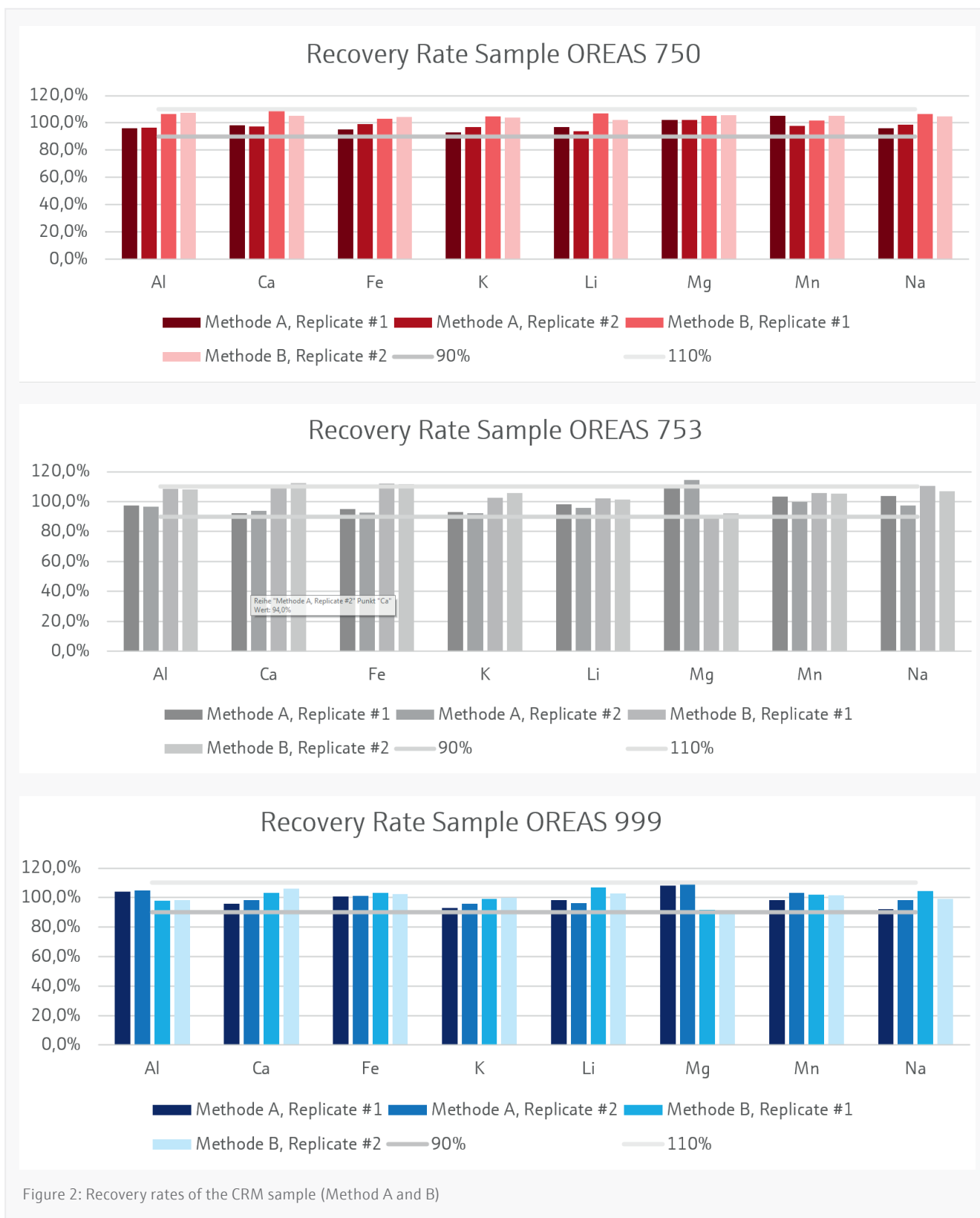
Table 5: Measuring results - Method B

Sample (CRM)	Element	DF	Certified value [wt%]	Replicate #1		Replicate #2	
				Measured value [wt%]	RSD _(n=3) [%]	Measured value [wt%]	RSD _(n=3) [%]
Oreas 750	Al	20	5.42	5.079	0.4	5.05	0.5
	Ca	20*	0.828	0.760	0.5	0.787	0.9
	Fe	20	1.67	1.619	1.2	1.598	0.4
	K	20	1.69	1.611	1.5	1.627	1.4
	Li	20	0.232	0.217	0.9	0.227	1.6
	Mg	20	0.315	0.299	0.6	0.298	1.0
	Mn	20	0.038	0.037	0.6	0.036	2.2
	Na	20*	1.53	1.437	2.6	1.458	2.9
Oreas 753	Al	20	8.22	7.582	0.1	7.594	0.6
	Ca	20	0.113	0.102	0.9	0.100	1.0
	Fe	20	0.839	0.749	1.4	0.751	1.2
	K	20	1.93	1.884	0.8	1.824	0.8
	Li	20	0.985	0.963	0.5	0.972	2.3
	Mg	20	0.011	0.012	2.4	0.012	2.1
	Mn	20	0.074	0.070	1.5	0.070	1.6
	Na	20*	2.16	1.957	0.6	2.019	0.3
Oreas 999	Al	20	10.77	11.0	0.4	10.96	1.2
	Ca	20	0.45	0.436	0.9	0.425	1.8
	Fe	20	1.62	1.569	1.2	1.584	0.6
	K	20	0.50	0.504	2.5	0.500	1.7
	Li	20	2.65	2.483	0.9	2.578	0.6
	Mg	20*	0.410	0.447	0.4	0.454	1.0
	Mn	20	0.143	0.140	1.7	0.141	0.9
	Na	20	0.693	0.665	0.9	0.698	1.8

RSD: Relative standard deviation (3 measurement replicates)

DF: Manual pre-dilution factor

*additional autosampler dilution due to exceeding the calibration range



The instrumental and method-specific limits of detection (LOD) and limits of quantification (LOQ) of the analysis are given in Table 6. These values were determined by using the reagent blank method (3- or 9-fold standard deviation of 11 repeated measurements of the reagent blank). The method-specific values were calculated according to the sample preparation (0.15 mg sample in 50 mL), including a sample pre-dilution factor of 20.

Table 6: Limits of detection (LOD) and limits of quantification (LOQ) considering the dilution factor of the method

Element	Instrument		Method-specific	
	LOD [$\mu\text{g/L}$]	LOQ [$\mu\text{g/L}$]	LOD [mg/kg]	LOQ [mg/kg]
Al	11.8	35.4	78.7	236
Ca	0.3	0.9	2.0	6.0
Fe	1.6	10.8	10.6	72
K	0.55	2.1	3.3	14
Li	0.18	0.6	1.3	3.9
Mg	0.8	2.4	5.3	16
Mn	0.55	2.1	3.3	9.9
Na	0.2	1.8	1.3	12

Summary

Equipped with a xenon short arc lamp as a continuum radiation source, the HR-CS flame AAS contrAA 800 F/D provides a reliable and easy to use technique for a fast sequential (approx. 6 elements in 2 min) multi-element analysis of major elements in digests of lithium ores. In combination with the autosampler AS-FD with intelligent dilution function (automatic preparation of calibration standards, overrange dilution), a fully automated routine analysis is enabled.

The measurement conditions were optimized to achieve the most uniform sample dilution possible. High concentrations of elements with sensitive absorption lines often require measures for decreasing the method sensitivity, such as a stronger sample dilution, usage of insensitive analysis lines or a burner head rotation. The side pixel evaluation tool of the contrAA software provides a comfortable and save option for improvement of the linearity range (see Figure 3) without interaction of the operator changing the burner head angle during the measurement sequence. Using the fast-sequential flame mode, which was also used in the application examples, the determination of elements can be applied in two multi-element methods, one for the acetylene/nitrous-oxide flame and one for the acetylene/air flame, both fully automatically running with flame ignition



Figure 3: contrAA 800 F with autosampler AS-FD

and shut down in one sequence. The measurement time is thus 3 - 4 times faster compared to classical AAS. Thus, the automation of the analysis process is improved and therefore, the contrAA 800 F/D can be seen as a cost-effective instrumental complement to other measurement techniques used for trace analysis.

Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
contrAA 800 F	815-08000-2	High-Resolution Continuum Source AAS (HR-CS) AAS for flame technique
Burner head NO/AC (50 mm)	810-60057-0	For acetylene/nitrous-oxide or acetylene/air flame
AS-FD	810-60501-0	Autosampler with auto-dilution function
Air compressor	810-60055-0 810-60053-0	50 Hz 60 Hz
Scraper	810-60127-0	For automatic burner head cleaning using acetylene/nitrous-oxide flame
Segmented Flow Star SFS 6.0	810-60129-0	Switching valve
Consumable set F	810-60258-0	Consumable set for flmae technique

Example for side pixel evaluation

This unique side pixel evaluation feature of the contrAA 800 is based on the high-resolution continuum source technique, where the spectral vicinity of the analysis line is included in the detection and recording. The ASpect CS software gives the experienced user the opportunity to customize

the evaluation of the absorption signal. This results in a maximum of flexibility, a significantly expanded working range over five orders of magnitude, and an analytical performance that can be optimized for the requirements of each application.

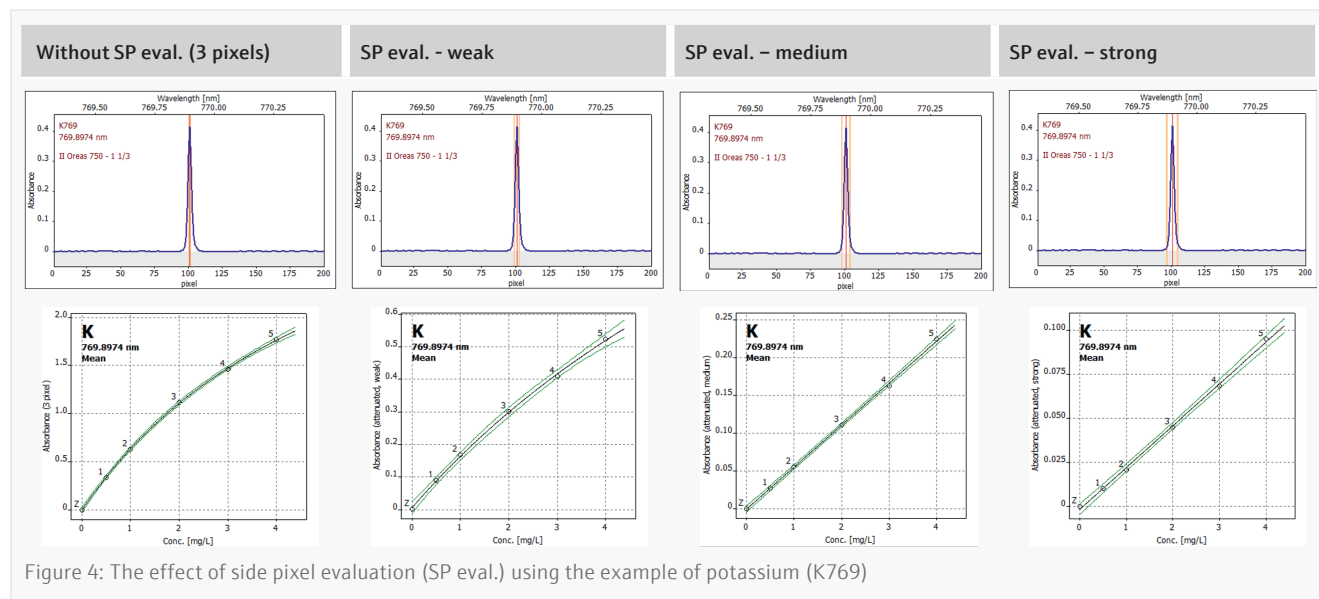


Figure 4: The effect of side pixel evaluation (SP eval.) using the example of potassium (K769)

References

- [1] Robert J. Bowell *et al.*; Classification and Characteristics of Natural Lithium Resources. *Elements* 2020; 16 (4): 259–264.

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